

## **DESCRIPTION**

5       **A procedure for the realisation of ceramic manufactures, in particular, porcelain stoneware tiles and trim pieces, with anti pollution and anti-bacterial properties and products thereby obtained.**

### **Technical field**

10      The invention relates to a procedure for the realisation of ceramic manufactures, in particular, porcelain stoneware, single-fired, monoporous or double-fired tiles and trims pieces with anti-pollution properties and products thereby obtained.

### 15      **Background Art**

For some time now, it has been common practice to produce manufactures with anti-bacterial and anti-pollution properties destined for the building industry with a wide range of applications such as, construction conglomerates, panelling for road networks and self-locking blocks for  
20      paving.

These manufactures are constituted, substantially, of a cement-based conglomerate whose mass contains particles of titanium dioxide,  $\text{TiO}_2$ , a property of which is its capacity to reduce the polluting agents present in the surrounding air.

25      Of these polluting agents, particular attention should be focussed on the polycyclic aromatic hydrocarbons (PAH) derived from the incomplete combustion of organic materials, wood, coal, oil, and its derivatives, and also the nitrogen oxides ( $\text{NO}_x$ ) present in the exhaust fumes from heating systems, industrial plants, motor vehicles, industrial wastes and pesticides.

30      The abatement of the level of environmental  $\text{NO}_x$  reduces both the possibility of acid rain and the presence of nitrates which are harmful to humans and vegetation. The bacteria which can be attacked by the presence of  $\text{TiO}_2$  include, for example, Staphylococci and Escheria Coli.

35      This result is due to the fact that the ultraviolet radiation of solar light, together with the humidity, interacts with the titanium dioxide particles, leading to the production of active oxygen which effectively oxidises the

aforesaid polluting and bacterial agents present in the atmosphere.

The products of the aforesaid oxidation are removed by water, either rainwater or washing water, and also by the alkaline nature of the cement conglomerates which, until now, have been realised with photocatalytic properties. Moreover, the aforesaid removal and elimination of the polluting products prevent their stagnation on the surface of the said manufactures, ensuring the original colours and their attractive appearance are maintained over time.

The drawback of the commonly-known manufactures with photocatalytic properties lies in the cement base of the said products which cause the said manufactures to have a rough surface and, consequently, limited possibility of high quality aesthetic variants and, consequently, limited possibility of application in the field of external wall coverings for the building industry.

Much higher aesthetic quality, for external wall coverings, is offered by manufactures of a ceramic nature, in particular porcelain stoneware tiles or those made of other pastes, such as single-fired or monoporos materials; however, until now, as far as the applicant is aware, no such material has been realised with polluting and antibacterial agent abatement properties. The main reason for this lies in the fact that the production of ceramic tiles requires firing treatments involving extremely high temperatures which, in the case of the porcelain stoneware manufactures, reach 1,200°C, unlike the production cycle of cement-based manufactures, which are produced by mixing and subsequent compaction, without requiring any thermal treatments.

It is known that when the  $\text{TiO}_2$  in the form of Anatase reaches 900°C, it is transformed entirely into Rutile, which, it has been demonstrated through experimentation, to be less effective than Anatase in particularly critical pollution situations such as on roads with a great deal of traffic. Moreover, it has been observed that, in the production phase, the transformation of Anatase into Rutile gives the glaze on ceramic manufactures a yellowish colour.

The applicant's studies have concentrated on the way in which the  $\text{TiO}_2$  can be made to coexist with the aforesaid extremely high temperatures without the decay of its photocatalytic properties, in addition to ensuring the photocatalytic effect of the ceramic tiles obtained in this way do not cause a decline in the high aesthetic quality of the said tiles.

The applicant's research and experiments have lead to different

considerations that are analysed hereunder.

The total presence of  $\text{TiO}_2$  in a finished tile (as a percentage thereof) which provides the best results varies within a range of 1-25% of the total weight of the applications (glazes, silk-screening, engobe, etc.). It should  
5 be highlighted that the photocatalytic reaction of the  $\text{TiO}_2$  to the polluting and bacterial agents does not involve the consumption of the said  $\text{TiO}_2$ , which means the efficacy of its action remains constant over time. It should also be noted that  $\text{TiO}_2$  can be mixed with both the glaze and the engobe (a covering formed of a thin layer of atomised clay applied to the  
10 partially dried clay) and can also be applied with the silk-screening pastes.

The effectiveness of the oxidation exerted by the  $\text{TiO}_2$  on the bacterial and polluting agents increases in the event that a photo-reflecting layer is applied, either beneath the layer of glaze covering the tile or with the said  
15 covering layer; for example, both white pigments and silica particles mixed with the glaze can be used; in this way, the rate at which the solar light penetrates the tiles is increased and this increases the photocatalytic effect exerted by the  $\text{TiO}_2$ .

It is known that  $\text{TiO}_2$  converts  $\text{NO}_x$  into nitrate ions which, upon oxidation, become Sodium and Calcium nitrates, which are not noxious,  
20 and which precipitate in the form of salts; the latter are removable by simply washing with water. From this came the idea that this washing action would be increased by an increase in the exposed surface, therefore the creation of micro channels on the surface of the tile would facilitate the action of the water (rain water or washing water) when removing the  
25 products of the oxidation caused by the pollutants.

In parallel, it was observed that the increase in the surface exposed to the light increases the photocatalytic effect of  $\text{TiO}_2$  and therefore it appeared  
evident to the applicant that it was also necessary to create, on the surface of the tiles, a plurality of non-uniform, micro uneven areas with the dual  
30 aim of permitting the solar light to hit the tiles from any direction and permit the air to better fix the  $\text{NO}_x$  which is decomposed by the ultraviolet radiation of the daylight.

To permit an efficacious retaining action of the gas developed during the night, while awaiting the daylight, the need to provide the tiles with  
35 materials able to store the said gas was considered. To this end, experimentation showed that the materials that absorb well are Zeolite and Petalite mixed with the glaze, or Magalite added to the traditional clays of which the tile base is composed.

**Disclosure of Invention**

The aim of this invention is to identify a procedure capable of enabling the production of ceramic manufactures, in particular porcelain stoneware, single-fired, monoporosa or double-fired tiles and trim pieces, with photocatalytic properties for the reduction of ambient pollution.

In particular, the procedure for the realisation of ceramic manufactures, in particular porcelain stoneware tiles and trim pieces, with anti-pollution properties, in question in this invention, is characterised by the fact that the said procedure, in combination with the production steps usual for the production of traditional ceramics, comprises the following phases:

- application of a variable percentage of  $\text{TiO}_2$  to the manufactures' engobe;
- application of a variable percentage of  $\text{TiO}_2$  to the covering glaze, the silk-screening pastes and the engobe;
- application, with the covering layer, of particles of material designed to increase the refraction of the solar light to which the manufactures are exposed;
- addition of substances designed to absorb  $\text{NO}_x$  to the covering layer and/or to the material of which the engobe is composed;
- creation of micro channels in the covering layer of the ceramic manufactures, said micro channels being designed to increase the permeability to water of the said manufactures;
- realisation of micro uneven areas in the aforesaid covering layer, said micro uneven areas being designed to increase the exchange surface between the single manufacture and the atmosphere;
- insufflation of air, on certain ramps of the kiln, during the traditional firing at  $1200^\circ\text{C}$ ; said insufflation being designed to produce an improvement in the photocatalytic effect of the  $\text{TiO}_2$ .

These and other characteristics will better emerge in the description that follows of a preferred embodiment illustrated, purely in the form of a non-limiting example.

After a first thermal treatment of a traditional type at low temperatures, designed, substantially, to facilitate the evaporation of at least part of the humidity present in the unfired tiles, the procedure continues with the application of the engobe and a glaze in which there is substantially 25%  $\text{TiO}_2$ , preferably in the form of Anatase; this application is carried out, preferably, by means of traditional methods (for example, a disk booth) or

by means of airbrushes without air with suitably modified nozzles.

There may be Magalite in the engobe.

There is silica sand mixed in with the glaze and, possibly, also white pigments. These materials may also be mixed in with the engobe.

- 5 The application of the  $\text{TiO}_2$  with the covering layer of the tiles, for example the silk-screening layer, envisages a presence of a percentage of the said  $\text{TiO}_2$ , limited to the materials constituting the said layer, which may vary, substantially, from 20% to 100%.

- 10 In the said glaze application phase, Zeolite and/or Petalite are added for the purpose of increasing the effect of the Magalite mixed in with the engobe.

Contemporaneously, and also in the aforesaid covering layer, micro channels and uneven areas are produced.

- 15 Finally, then, during the application of the covering layer, using silk-screening machines of a commonly known type, four operations are performed contemporaneously by means of the use of four synchronised silicon rollers, in the following order: a first roller creates the micro uneven areas on each tile base, a second roller applies the substance(s) designed to increase the absorption of  $\text{NO}_x$ , a third roller applies the material designed to increase the refraction and a fourth roller compacts everything, redefines the micro uneven areas and produces the micro channels.

- 20 At this point, the definitive firing takes place, the said firing being of the traditional type as regards the temperature, which, for porcelain stoneware ceramic material, reaches around  $1,200^\circ\text{C}$ , but in the procedure in question in this invention, envisages a modification consisting in an insufflation of air directly into the firing kiln; said insufflation involves the use of a system of shutters positioned directly above the kiln and operated by software which controls, at the same time, the oxidation, the quantity of  $\text{CO}_2$  and the  $\text{TiO}_2$  melting point.

- 30 As the last phase of the procedure in question in this invention, a re-firing of the tiles may be effected at approximately  $600^\circ\text{C}$ , subject to the application, to the tiles fired the first time, of a thin layer of crystalline containing  $\text{TiO}_2$ .

- 35 Over the course of the description, explicit reference has also been made to porcelain stoneware ceramic tiles as the ceramic manufactures, but the procedure in question in this invention can quite evidently also be applied, advantageously, to ceramic tiles of a different type, for example single-

fired, monoporously, double-fired, clinker tiles etc.

Moreover, over the course of the description, explicit reference has been made to tiles, but it is evident that the procedure in question in this invention is applicable, advantageously, to any type of ceramic product regardless of the form and dimensions.

The applicant has proceeded with the production of three classes of porcelain stoneware tiles:

- a) a tile without any modifications to the traditional firing and with the presence of  $\text{TiO}_2$  essentially in the form of Rutile;
- b) a tile obtained with the modification of the firing phase by means of the insufflation of air, intervening during the transformation of Anatase into Rutile;
- c) a tile, as in the previous point, but with the addition of a layer of  $\text{TiO}_2$  after firing is complete. Tests have also been carried out in which this last typology of tile undergoes a re-firing at  $600^\circ\text{C}$  with the aim of improving the fixing of the  $\text{TiO}_2$  still further.

The three typologies of tiles just mentioned underwent efficiency tests which lead to the conclusion that  $100\text{m}^2$  of treated tiles, with particular reference to those in typology c), can clean a volume of air of approximately  $15,000\text{m}^3$  during a sunny day.

There will now follow a list of the production characteristics of the five embodiments originating from the aforesaid three tile typologies.

A first porcelain stoneware manufacture was obtained with the following production characteristics:

- engobe with 25%  $\text{TiO}_2$  applied by means of an airbrush without air, functioning under high pressure;
- serigraphy using iron molybdate;
- calcic glaze with 25%  $\text{TiO}_2$  applied by means of an airbrush without air, functioning under high pressure;
- application of 100%  $\text{TiO}_2$  by silk-screening.

A second porcelain stoneware manufacture was obtained with the following production characteristics:

- engobe with 25%  $\text{TiO}_2$  applied by means of a disk booth;
- silk-screening using iron molybdate;
- zinc glaze with 25%  $\text{TiO}_2$  applied by means of an airbrush without air, functioning under high pressure;
- application of 100%  $\text{TiO}_2$  by silk-screening.

A third porcelain stoneware manufacture was obtained with the following

production characteristics:

- engobe with 25%  $\text{TiO}_2$  applied by means of a disk booth;
- silk-screening using iron molybdate;
- glossy alkaline silica-boron glaze with 25%  $\text{TiO}_2$  applied by means of an airbrush without air, functioning under high pressure;
- application of 100%  $\text{TiO}_2$  by silk-screening.

A fourth porcelain stoneware manufacture was obtained with the following production characteristics:

- engobe with 25%  $\text{TiO}_2$  applied by means of an airbrush without air, functioning under high pressure;
- silk-screening using iron molybdate;
- glossy silica-boron-zirconium glaze with 25%  $\text{TiO}_2$  ;
- application of 100%  $\text{TiO}_2$  by silk-screening.

A fifth porcelain stoneware manufacture was obtained with the following production characteristics:

- engobe with 25%  $\text{TiO}_2$  applied by means of an airbrush without air, functioning under high pressure;
- silk-screening using iron molybdate;
- application of 100%  $\text{TiO}_2$  by means of an airbrush without air, functioning under high pressure;
- application of 100%  $\text{TiO}_2$  by silk-screening.

The advantage of the procedure in question in this invention consists in the fact that it enables the realisation of ceramic manufactures for finishing in the building industry capable of developing a photocatalytic oxidising action against polluting and bacterial agents.